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**Carbonaceous
aerosols in six
European cities**

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Comparison of the levels of organic, elemental and inorganic carbon in particulate matter in six urban environments in Europe

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A series of 7-week sampling campaigns were conducted in urban background sites in the six European cities as follows: Duisburg 4 October–21 November 2002 (autumn), Prague 29 November 2002–16 January 2003 (winter), Amsterdam 24 January–13 March 2003 (winter), Helsinki 21 March–12 May 2003 (spring), Barcelona 28 March–19 May 2003 (spring) and Athens 2 June–21 July 2003 (summer). The campaigns were scheduled to include seasons of local public health concern due to high PM concentrations or findings in previously conducted epidemiological studies. Aerosol samples were collected in parallel with two identical virtual impactors (VI), which divide air PM into two size fractions, $PM_{2.5}$ and $PM_{2.5-10}$. The filter samples were analysed with a microbalance, an energy dispersive X-ray fluorescence (ED-XRF), an ion chromatograph (IC) and a thermo-optical carbon analyser (TOA). The $PM_{2.5}$ and $PM_{2.5-10}$ campaign means ranged $8.3\text{--}29.6\text{ }\mu\text{g m}^{-3}$ and $5.4\text{--}28.7\text{ }\mu\text{g m}^{-3}$, respectively. The “wet and cool” seasons favoured low coarse PM concentration and high fine PM concentration, whereas the spring and summer led to low fine and high coarse PM concentrations. The contribution of particulate organic matter (POM) to $PM_{2.5-10}$ was highest (27%) in Prague and the lowest (10%) in Barcelona, while those to $PM_{2.5}$ were generally higher, ranging from 21% in Barcelona to 54% in Prague. The contribution of elemental carbon (EC) to $PM_{2.5-10}$ were relatively low (1–6%) in all the six European cities but it contributed somewhat higher (5–9%) to $PM_{2.5}$. The differences are most likely due to variable contributions of local emission sources and seasonal factors such as domestic heating, vehicle exhausts and photochemical reactions. Carbonate, which interferes with carbon analysis by evolving stage at 900°C , was detected in the coarse particles of Athens and Barcelona and it could be separated reliably from OC by a simple integrating method. The calcium carbonate in Athens and Barcelona accounted for 56% and 11% of coarse PM masses, respectively. Carbonate was not found in other cities or in $PM_{2.5}$. The mean $PM_{2.5}$ mass portions of five OC thermal fractions (OC1, OC2, OC3, OC4 and OCP) varied in the range 26–33%, 6–10%, 7–10%, 9–22% and

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29–50%, respectively, in six cities. The differences in the mass portion profiles were relatively small between the cities.

1. Introduction

Urban aerosol is a complex mixture of primary particulate emissions (from industry, transportation, power generation and natural sources) and secondary material formed by gas-to-particle conversion mechanisms. Tropospheric aerosols contain sulphate, ammonium, nitrate, sea salt, trace metals, carbonaceous material, crustal compounds and water. Carbonaceous constituents such as elemental carbon (EC) and organic compounds usually have large contributions to the mass of all PM₁₀ subfractions. EC (sometimes referred to as black carbon or graphitic carbon) is a primary pollutant formed in combustion processes, but particulate organic matter (POM) is a complex mixture of many groups of compounds originating from a large variety of processes (Seinfeld and Pandis, 1998).

Recent epidemiological studies have shown consistent associations of mass concentration of urban air thoracic particles (PM₁₀–50% cutoff point at 10 µm), and its sub-fraction fine particles (PM_{2.5}–50% cutoff point at 2.5 µm), with mortality and morbidity among cardiorespiratory patients (WHO, 2003). There are still relatively few epidemiological studies with chemical speciation of the collected particulate samples, but one recent US time-series study (Metzger et al., 2004) has reported that the EC and POM concentrations in PM_{2.5} were significantly associated with emergency department visits in hospitals due to cardiovascular conditions. EC causes tissue irritation and the release of toxic chemical intermediates from scavenger cells in laboratory studies as well as acts as an carriers for various organic compounds. Volatile and semi-volatile organic chemicals associated with the particles can act as irritants and allergens. Many aromatic compounds are suspected mutagens and carcinogens and some them may also acute effects (Lighty et al., 2000).

In this study, we report the mass concentrations of fine (PM_{2.5}) and coarse (PM_{2.5–10})

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particles as well as their EC and POM contents from particulate sampling campaigns in six European cities. The specific objective of our work has been to characterise the differences in these particulate constituents between purposefully selected contrasting air pollution caused by variations in emission sources, geographical location and season. Moreover, the campaigns were scheduled to include seasons of local public health concern due to high PM concentrations or findings in previously conducted epidemiological studies.

2. Experimental methods

2.1. Sampling sites

A series of 7-week sampling campaigns were conducted in six European cities. The sampling sites (Fig. 1) were located in urban background areas and were influenced by variable contribution of traffic depending on the density of short-haul traffic and the local topography of site. The sites are described in detail including the additional local emission sources:

Duisburg (51°26' N, 6°45' E). The sampling site was located near the city centre at a distance of 280 m from the nearest major street. The site was surrounded by three to five-storey buildings. The major local emission sources were traffic (e.g. diesel trucks) and metal industry. The sampling campaign was carried out between 4 October and 21 November 2002 (autumn) when the mean±SD ambient temperature and total precipitation were 9±3°C and 90 mm.

Prague (50°5' N, 14°26' E). The sampling station was located on the open field of Czech Hydrometeorological Institute in an uptown residential area. The nearest road was at a distance of 150 m with an average traffic density of 5000 vehicles/day, while the nearest major road was at a distance of 1 km. Traffic, domestic heating with solid fuels and energy production were the main local emission sources. The samplings were carried out between 29 November 2002 and 16 January 2003 (winter) when the

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mean±SD ambient temperature and total precipitation were $-2\pm5^{\circ}\text{C}$ and 50 mm.

Amsterdam ($52^{\circ}21' \text{N}$, $4^{\circ}54' \text{E}$). The site was located near the city centre at a distance of 50 m from the nearest major street with an average traffic volume of 10 000 vehicles/day. The site was surrounded by multi-storey buildings. Traffic and sea were the main local emission sources. The samplings were carried out between 24 January and 13 March 2003 (winter) when the mean±SD ambient temperature and total precipitation were $4\pm4^{\circ}\text{C}$ and 60 mm.

Helsinki ($60^{\circ}10' \text{N}$, $24^{\circ}58' \text{E}$). The site was located near the city centre at a distance of 300 m from the nearest street with an average traffic volume of 30 700 vehicles/day. The site had multi-storey buildings on one side, but faced an open-air sports field on the other side. Traffic and ships in harbour were the main local emission sources. The samplings were carried out between 21 March and 12 May 2003 (spring) when the mean±SD ambient temperature and total precipitation were $4\pm5^{\circ}\text{C}$ and 48 mm.

Barcelona ($41^{\circ}23' \text{N}$, $2^{\circ}9' \text{E}$). The site was located on a car park near the city centre. The nearest road was at a distance of 100 m with an average traffic density of 17 000 vehicles/day. On one side there was a multi-storey building and the canopy of a railway station whilst on the other side there was a park enclosing a zoo. The main local emissions originated from traffic and harbour as well as the zoo to some extent. The samplings were carried out between 28 March and 19 May 2003 (spring) when the mean±SD ambient temperature and total precipitation were $15\pm2^{\circ}\text{C}$ and 10 mm.

Athens ($37^{\circ}58' \text{N}$, $23^{\circ}43' \text{E}$). The site was located near the city centre at a distance of 100 m from the nearest road with an average traffic density of 30 000 vehicles/day. The site was spaciouly enclosed with three- or four-storey buildings. The main local sources were traffic and construction work to some extent. The samplings were carried out between 2 June and 21 July 2003 (summer) when the mean±SD ambient temperature and total precipitation were $29\pm4^{\circ}\text{C}$ and 0 mm.

The sampling durations were 3 or 4 days in alternation, with sample exchange usually in Mondays and Thursdays between 10 and 12 a.m. The total number of samplings was 14 in each city. The automatic valve, that was programmed to switch on and off in

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the cycles of 15 min, was set into the pump line of virtual impactors (VI) in Barcelona and Athens to avoid an overloading of the filters.

2.2. Aerosol sampling instruments

5 Aerosol particle samples were collected in parallel with two identical virtual impactors (VI; Loo and Cork, 1988). The VI divided airborne particulate matter into two size fractions: PM_{2.5} and PM_{2.5-10}. Particles were collected on polytetrafluoroethylene (PTFE) filters (diameter 47 mm, pore size 3 μm, type FS, Millipore, Ireland) for gravimetric analysis and on preheated quartz fibre filters (Pallflex Tissuquartz 2500QAT-UP) for carbon analysis. In the latter VI, a tandem filter collection method (two quartz fibre filters from
10 the same lot in series) was applied to estimate and correct for the positive sampling artefacts, i.e. the absorption of organic gases. The total sampling flow rates of the VIs were 16.7 l min⁻¹ and the upper cut-off sizes of the coarse fraction was established with a low volume PM₁₀-inlets similar to the design of Liu and Pui (1981).

2.3. Gravimetric and chemical analysis

15 After sampling, the filters were placed in petrislides and those containing the quartz fibre filters were wrapped inside aluminium foil. All the samples were frozen and sent via express delivery service to a central laboratory of the project for further analyses.

The PTFE filters were weighed with a Mettler M3-microbalance (Mettler Instrumente AG, Zurich, Switzerland) before sampling and before any chemical analysis. The samples were allowed to become stabilized in the weighing room for 15–60 min before weighing. Weighings were considered valid if duplicate mass readings were within 2 μg of each other. The relative humidity (RH) and temperature in the weighing room were 22±7% and 23±2°C, respectively, with the exception of RH being 49±8% during the weighings of Barcelona- and Athens-samples. Regardless of different RH, the deliquescence points of the abundant atmospheric inorganic salts were reached neither
25 at 22% nor at 49% (Seinfeld and Pandis, 1998), because the filter samples (stored as

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frozen) were melted and then stabilized at the prevailing condition of weighing room. The scale and the reading of the microbalance were checked daily by using internal and standard weights, respectively. The electrostatic charges of filters and substrates were eliminated by using a Po-210 radioactive source.

5 The quartz fibre filters were analysed using a thermal-optical carbon analyser (TOA; Sunset Laboratory Inc., Oregon). This analysis proceeds in two stages. In the first stage, organic carbon (OC) and carbonate carbon are volatilized in pure helium atmosphere at four temperature steps. During the second stage of the analysis, the carbon remaining on the filter is heated in the mixture of oxygen and helium (1:49, V-%) by
10 using six temperature steps. The temperature program is shown in Table 1. A part of OC is pyrolysed into compounds resembling the EC during the heating. An optical correction, i.e. a measurement of the transmittance of laser light through the filter, is applied to identify the pyrolysed OC from the EC that is determined to be the fraction of carbon that comes out after the transmittance has reached its initial value. The POM
15 is obtained by summing the OC peaks and pyrolysed OC and multiplying the sum by a factor of 1.4 (Turpin et al., 2000 and Russell, 2003). An analogous method has been described in detail by Viidanoja et al. (2002).

The carbonaceous material is divided into six thermal fractions (Fig. 4). Hereafter in this paper, those thermal fractions are labelled as follows: OC1 (310°C), OC2 (480°C),
20 OC3 (615°C), OC4 (900°C), OCP (pyrolysed OC) and EC (sum of EC thermal fractions). C(CO₃) refers to the carbonate carbon. The water-solubility of OC thermal fractions increases from left to right.

The total concentration and water-soluble fraction of calcium was determined from the PTFE filters by using an energy dispersive x-ray fluorescence (ED-XRF; Tracor Spectrace 5000) and an ion chromatography (IC; Dionex DX500, Dionex Corporation,
25 Sunnyvale, USA). The ED-XRF method has been described in detail by Spolnik et al. (2004) and the data analysis code has been published by Vekemans et al. (1994). The accuracy and precision of the present ED-XRF analysis are on average 14% and 4%, respectively. The IC method is described by Teinilä et al. (2000) and its uncertainty

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for calcium is estimated at 10%.

The CaCO_3 concentrations were converted from those of CO_3^{2-} and Ca^{2+} – based on the TOA and the ED-XRF analysis, respectively – by using the following equations:

$$[\text{CaCO}_3]_{\text{TOA}} = \frac{M(\text{CaCO}_3)}{M(\text{C}(\text{CO}_3))} [\text{C}(\text{CO}_3)] = 8.334 \times [\text{C}(\text{CO}_3)] \quad (1)$$

$$[\text{CaCO}_3]_{\text{XRF}} = \frac{M(\text{CaCO}_3)}{M(\text{Ca})} [\text{Ca}] = 2.497 \times [\text{Ca}], \quad (2)$$

where $[\text{C}(\text{CO}_3)]$ and $[\text{Ca}]$ are the mass concentration of carbonate carbon and calcium, respectively.

The area of carbonate peak in TOA thermograms was manually integrated by setting the integral start to 210–225 s and the integral end to 250–275 s.

3. Results and discussion

3.1. $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ mass concentrations

The mean mass concentrations of $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ during the 7-week campaigns in the six European cities are shown in Fig. 2. The concentrations were 14.7 and $7.2 \mu\text{g}/\text{m}^3$ in Duisburg, 29.6 and $5.4 \mu\text{g}/\text{m}^3$ in Prague, 25.4 and $8.4 \mu\text{g}/\text{m}^3$ in Amsterdam, 8.3 and $12.8 \mu\text{g}/\text{m}^3$ in Helsinki, 20.0 and $26.3 \mu\text{g}/\text{m}^3$ in Barcelona, and 25.3 and $28.7 \mu\text{g}/\text{m}^3$ in Athens, respectively. The highest mean $\text{PM}_{2.5}$ concentration was measured in Prague during winter and the highest mean $\text{PM}_{2.5-10}$ concentration was measured in Athens during summer, whereas the corresponding lowest values were in Helsinki during spring and in Prague during winter. For comparison (data from local authorities), the annual mean $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ mass concentrations in 2001 were, respectively, as follows: 23.0 and $6.8 \mu\text{g}/\text{m}^3$ in Duisburg, 7.8 and $7.9 \mu\text{g}/\text{m}^3$ in Helsinki, and 28.0 and $13.0 \mu\text{g}/\text{m}^3$ in Barcelona. These two PM size fractions were not

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measured in the other three cities but the annual mean PM_{10} mass concentrations in 2001 were $24.5 \mu\text{g}/\text{m}^3$ in Prague, $28.9 \mu\text{g}/\text{m}^3$ in Amsterdam and $55.5 \mu\text{g}/\text{m}^3$ in Athens. Our sampling campaign means were clearly higher than the corresponding annual means for Prague- PM_{10} (43%), Amsterdam- PM_{10} (17%), Helsinki- $\text{PM}_{2.5-10}$ (62%) and Barcelona- $\text{PM}_{2.5-10}$ (100%), confirming special episodes/seasons in these cities during the campaigns. No difference with the historical annual mean value was found for Duisburg- $\text{PM}_{2.5-10}$ (5.9%), Helsinki- $\text{PM}_{2.5}$ (6.4%) and Athens- PM_{10} (−2.7%), but our campaign means were clearly lower than the annual means of 2001 for Duisburg- $\text{PM}_{2.5}$ (−36%) and Barcelona- $\text{PM}_{2.5}$ (−29%).

The mean $\text{PM}_{2.5-10}$ to $\text{PM}_{2.5}$ ratios were significantly lower in Duisburg (0.58), Prague (0.20) and Amsterdam (0.54) than in Helsinki (1.57), Barcelona (1.36) and Athens (1.14). According to their mass size fractions, the sampling campaigns could be roughly divided into two groups: one with dominating fine fraction and the other with dominating coarse fraction. The variations were most likely explained by differences in season, local emission sources and geographical location. The first three sampling campaigns were carried out during the ‘wet’ and cool season favouring low coarse PM concentration (due to low resuspension) and high fine PM concentration (additional local and regional energy production for heating). The sampling campaigns in Barcelona and Athens were conducted during warmer and drier seasons leading to lower fine PM concentration (semivolatiles in gas phase) and high coarse PM concentration (resuspension). Road dust episodes, typical phenomena in springtime, are the reason for elevated coarse PM concentration in Helsinki. More detailed data on the PM mass concentrations, meteorology and air quality during these sampling periods will be reported elsewhere.

3.2. Mass concentrations of EC and POM in six cities

The mean POM and EC mass concentrations in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ of the six-city samples are shown in Fig. 3. The POM mean ($\pm\text{SD}$) concentrations in $\text{PM}_{2.5}$

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varied profoundly between $3.8(\pm 1.4) \mu\text{g m}^{-3}$ in Helsinki and $15.7(\pm 7.2) \mu\text{g m}^{-3}$ in Prague, while the corresponding EC concentrations varied much less, i.e. between $0.68(\pm 0.25) \mu\text{g m}^{-3}$ in Helsinki and $1.6(\pm 0.2) \mu\text{g m}^{-3}$ in Athens. The mean POM (corrected for carbonate, see 3.3.1) and EC mass concentrations in $\text{PM}_{2.5-10}$ varied in the range 1.2–6.8 $\mu\text{g m}^{-3}$ and 0.18–0.28 $\mu\text{g m}^{-3}$, respectively. The lowest mean POM and EC in $\text{PM}_{2.5-10}$ were observed in Amsterdam, while the corresponding highest concentrations were in Athens. The mean OC concentrations on $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ backup filters varied in the range 0.32–1.31 and 0.12–0.33 $\mu\text{g m}^{-3}$, contributing 5.7–19% and 5.8–14% of the OC on the front filter, respectively. The corresponding EC contributions were about one tenth of those of OC, which was also anticipated because of the nonvolatile nature of elemental carbon.

In this study, the POM of both fine and coarse fractions was obtained by multiplying organic carbon with a factor of 1.4 in each city. The conversion was applied to estimate the sum of mass concentration of organic compounds (POM), not only their carbonaceous content (OC) (Turpin et al., 2000 and Russell, 2003). Although in reality the POM to OC ratio alters between the different samples, this factor was used due to the limitations of present instruments (e.g. FTIR spectroscopy or GC/MS).

Querol et al. (2004) reported in their European multi-city study that the annual mean $\text{PM}_{2.5}$ mass concentrations of total carbon (TC; sum of OC and EC) varied in the range of 2–8 $\mu\text{g m}^{-3}$ in the urban background sites. Our campaign-mean TC concentrations of $\text{PM}_{2.5}$ fell into this range everywhere except in Prague ($12.6 \mu\text{g m}^{-3}$), where the exceedance was most likely due to the emissions from additional local residential heating with solid fuels (coal, biomass) and additional regional energy production during winter season. In Querol et al. (2004), the annual mean TC mass concentrations of $\text{PM}_{2.5-10}$ ($\text{PM}_{2.5-10} = \text{PM}_{10} - \text{PM}_{2.5}$) varied in the range of 0–1 $\mu\text{g m}^{-3}$, while our campaign-mean TC were between 1.0 and 1.9 $\mu\text{g m}^{-3}$, except that it was as high as 3.9 $\mu\text{g m}^{-3}$ in Athens.

It is worthwhile noting here that the EC and OC concentrations are dependent on

the method used in thermal-optical carbon analysis. Chow et al. (2001) showed that the NIOSH and IMPROVE methods (Table 1) are equivalent for total carbon but the EC-NIOSH (usually a smaller fraction of TC) typically gives less than half of the values of the EC-IMPROVE. A reasonable estimation for EC lies between these two methods (Sciare et al., 2003). The method used in this study was a NIOSH method with minor modifications, and therefore the EC concentrations could be underestimated.

The contributions of carbonaceous materials to $PM_{2.5}$ and $PM_{2.5-10}$ are shown in Table 2. As expected, the EC contributions to $PM_{2.5-10}$ (1–6%) were lower than to $PM_{2.5}$ (5–9%) in all the six European cities. The POM contribution to $PM_{2.5-10}$ was highest (27%) in Prague and lowest (10%) in Barcelona, while those to $PM_{2.5}$ were generally higher, ranging from 21% in Barcelona to 54% in Prague. The differences are most likely due to variable contributions of local emission sources and seasonal factors such as residential heating with solid fuels, vehicle exhausts and photochemical reactions. Putaud et al. (2004) averaged out the mean annual black carbon (BC) and POM contributions based on the measurements in eight European cities (urban background sites). The mean BC contributions to $PM_{2.5}$ and $PM_{2.5-10}$ ($=PM_{10}-PM_{2.5}$) were 8% and 3%, respectively, which agreed well with our results. In contrast, their annual mean POM contributions to $PM_{2.5}$ and $PM_{2.5-10}$ were 22% and 8%, being similar to the minimum values of our campaign-means and only about one-third to one-half of our maximum values.

The mean (\pm SD) $PM_{2.5}$ to PM_{10} proportions of elemental carbon varied between 78(\pm 6)% and 86(\pm 6)%. These high percentages indicate that EC existed mainly in fine particulate fractions, which was expected since EC is produced only in combustion processes. The mean $PM_{2.5}$ to PM_{10} ratios of POM varied more than those of EC. The mean POM percentages (\pm SD) were 56 \pm 4% in Athens, 65 \pm 6% in Barcelona, 68 \pm 8% in Helsinki, 71 \pm 11% in Duisburg, 81 \pm 6% in Amsterdam and 92 \pm 4% in Prague. The proportions increased with the decreasing mean ambient temperature during the sampling campaigns, which could be explained by e.g. the fact that during warm seasons traffic-derived semivolatile organics favour appearance mainly in the gas phase,

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energy production for heating decreases and there are higher natural emissions of coarse POM.

5 The OC to EC ratios of fine particulate size fraction varied in the range of 2.1–4.3 in Barcelona, Duisburg, Athens, Helsinki and Amsterdam, whereas it was apparently higher (8.7) in Prague. Na et al. (2004) have reviewed some reported OC/EC ratios. The low OC/EC ratio has been associated with traffic sources (2.2 and 0.8 for light-duty gasoline and heavy-duty diesel vehicles, respectively), whereas residential heating (residential wood combustion 4.15 and natural gas home appliance 12.7), forest fire (14.5) and paved road dust (13.1) have caused remarkably higher ratios. On the other hand, it is noteworthy that the analysis method is critical for the division between OC and EC. In view of the ratios above, residential heating could have a significant impact on the high OC in Prague, whereas traffic played an important role in other cities.

10 The Pearson's correlation coefficients between particulate mass concentration, POM, and EC in both $PM_{2.5}$ and $PM_{2.5-10}$ are shown in Table 3. The $PM_{2.5}$ mass concentration had a strong correlation ($r=0.84-0.99$) with fine POM in all the cities except in Barcelona ($r=0.57$) where the POM had a small contribution to $PM_{2.5}$. However, fine POM correlated well ($r=0.95$) with fine EC in Barcelona, which together with the low OC/EC (2.1) suggests that they had a common dominant source different from the other cities, e.g. oil combustion in ship engines at the large harbour. The coarse POM correlated well ($r\geq 0.90$) with coarse particulate mass in both Prague and Helsinki, and with both fine POM and coarse EC in Amsterdam.

3.3. Analysis of thermal fractions

3.3.1. Carbonates in atmospheric particles

25 Carbonate can interfere with the carbon analysis by evolving during the OC4 step ($900^{\circ}C$; Fig. 4), thus causing a positive artefact to the OC concentration (Sciare et al., 2003). In this study, the carbonate could be quantified in $PM_{2.5-10}$ of Barcelona and Athens but it could not be detected neither in $PM_{2.5-10}$ of the other four cities nor

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in $\text{PM}_{2.5}$ of any city. The $\text{C}(\text{CO}_3)$ to OC ratio in coarse particles was on average 0.17 in Barcelona and 0.53 in Athens, which shows that the OC (or POM) concentration would have been largely overestimated without the exclusion of $\text{C}(\text{CO}_3)$. The concentration of carbonate carbon ($\text{C}(\text{CO}_3)$) was subtracted from the sum of the OC total area for the POM results shown in Sect. 3.2.

The time series of CaCO_3 concentrations in $\text{PM}_{2.5-10}$ from Athens and Barcelona are shown in Fig. 5. The campaign mean (range), based on Eq. (1), was 15.9 (9.8 – 29.2) $\mu\text{g m}^{-3}$ in Athens whereas the corresponding value in Barcelona was 2.6 (0.3 – 6.3) $\mu\text{g m}^{-3}$. These concentrations accounted for $56(\pm 9)\%$ and $11(\pm 9)\%$ of the coarse particulate mass in Athens and Barcelona, respectively. The $[\text{CaCO}_3]_{\text{TOA}}$ and $[\text{CaCO}_3]_{\text{XRF}}$ (based on Eqs. 1 and 2) match up well in Athens (Pearson's $r = 0.91$), as well as there is a trend in Barcelona (Pearson's $r=0.61$) but the molar equivalent concentration of CO_3^{2-} was lower than that of Ca^{2+} . This indicates that the coarse calcium exists exclusively as carbonate in Athens, whereas the coarse calcium in Barcelona partly exists also in other forms (e.g. as oxide). The similar conclusion was also drawn by Bardouki et al. (2003) who discovered according to ion balance that the calcium in coarse mode was strongly associated with carbonate (a molar ratio of unity) in the Eastern Mediterranean in summertime.

Figure 6 depicts the occurrence and proportions of crustal elements in six cities. Calcium had a major contribution in Barcelona and Athens, whereas aluminium or silicon dominated in other four cities. In addition, based on the mass size distribution measurements by Berner low pressure impactor and on the IC analysis (data not shown), the PM_{10} calcium existed almost exclusively in $\text{PM}_{2.5-10}$ in both Barcelona ($93\pm 4\%$) and Athens ($89\pm 2\%$) as well as in other cities (75 – 86%). The contribution of watersoluble fraction to the total amount of calcium was determined by comparing the concentration measured by the IC (soluble fraction) to that measured by the ED-XRF (total amount). Low coarse Ca concentration together with its high water-solubility in Duisburg, Prague and Amsterdam indicate that calcium exists as water-soluble compounds (e.g. as oxide or sulphate) and calcium carbonate had an exiguous contribution to particulate mass.

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On the contrary, high coarse Ca suggested to the presence of calcium carbonate in Barcelona and Athens; in the latter city main fraction of calcium was water-insoluble. The poor water-solubility of calcium in Helsinki indicated to the presence of calcium carbonate or calcium silicates, though carbonate could not be detected most likely due to its low concentration.

These results indicate that in the thermal-optical carbon analysis the carbonate can be reliably excluded from the OC and therefore this integration method can be used as an alternative for the HCl pre-treatment method (Cachier et al., 1989).

3.3.2. Thermal fraction of OC in PM_{2.5}

The thermograms, i.e. the output of EC/OC analysis, are commensurate between the six-city samples, since the results were produced by following the identical sampling and analytical methods. The mean PM_{2.5} mass portions of the five OC thermal fractions, labelled OC1, OC2, OC3, OC4 and OCP, varied in the range 26–33%, 6–10%, 7–10%, 9–22% and 29–50%, respectively, in the six cities (Fig. 7). The differences in the mass portion profiles were relatively small between the cities. However, a distinct observation was that the pyrolysed fraction of total OC was higher (50%) in Prague than in the other cities (29–41%) and, vice versa, the OC peaks at temperature steps of 480, 615 and 900°C were smaller in Prague than in the other cities. In addition, the OC1 fraction (at 310°C) was 33% for both Barcelona and Athens while it was somewhat lower (26–29%) for the other cities.

The fine OC correlated inversely with OC1 ($r=-0.32-0.75$), OC2 ($r=-0.022-0.58$), OC3 ($r=-0.51-0.69$) and OC4 ($r=-0.31-0.94$) in any city, whereas the OCP correlated well with OC ($r=0.70-0.93$). This is more likely due to an insufficiently long residence time at each temperature step of the TOA method, which increases the charring of OC (Yu et al., 2002) than due to the different composition of organic species. The transmittance of laser light through the filter decreased gradually during each OC temperature step (OC1-OC4), which suggests that OC pyrolysed all along the helium stage.

The dominating thermal fraction of the PM_{2.5} backup filters was OC1 (56–62%), while

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the OC2-OC4 (10–16%) and the OCP were equally found only in minor amounts (0–3%). The thermogram profiles were congruent between the cities and irrespective of geographical location or season. In this study, the OC on the backup filter is supposed to be comprised of the absorption of organic gases, but some part of it may have been formed from the evaporation of the particles collected on the front filter (Turpin et al., 2000). Regardless of its origin (positive or negative artefact), the OC on backup filter should be easily volatile, which can be also seen in our results.

The advantages of this study were that 1) all the samples were collected by following a uniform protocol and they were analysed by using the same thermo-optical method, which allowed us to take a comparative look at the six-city results and 2) the long sampling time and the use of filters from one manufacturing lot improved the accuracy of the tandem quartz filter subtraction method (Kirchstetter et al., 2001). Nevertheless, only very limited conclusions can be drawn from the chemical content of thermal fractions, because the evolution of organic components depends on the several factors: First, the presence of some catalytically active inorganic salts such as Na^+ and K^+ (Novakov and Corrigan, 1996) or ammonium sulphate and phosphate (Yu et al., 2002) can increase the combustion rate of certain compounds (Novakov and Corrigan, 1996) or the charring of insoluble organic materials (Yu et al., 2002). Second, as mentioned above, the too short steps of temperature program cause the overlapping of OC peaks and increase the OC charring. Third, organic gases can be adsorbed on quartz filter with more than a single binding energy (Kirchstetter et al., 2001) which results in the evolution of single compound to the various thermal fractions.

4. Summary and conclusions

A series of 7-week sampling campaigns were carried out during selected seasons at the different locations in Europe: Duisburg (autumn), Prague (winter), Amsterdam (winter), Helsinki (spring), Barcelona (spring) and Athens (summer). The $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ samples were collected simultaneously with two identical virtual impactor and

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they were analysed with a microbalance, energy dispersive X-ray fluorescence, an ion chromatograph and a thermal-optical carbon analyser.

We showed large differences in $PM_{2.5}$ and $PM_{2.5-10}$ concentrations between the selected urban air pollution situations in Europe. The “wet and cool” seasons favoured low coarse PM concentration and high fine PM concentration, whereas the spring and summer led to low fine and high coarse PM concentrations. There were additional differences in the POM to mass ratio in both $PM_{2.5}$ and $PM_{2.5-10}$, suggesting variations in local emission sources and seasonal factors such as domestic heating, vehicle exhausts and photochemical reactions. The high fine POM in Prague was most likely due to the emissions from additional local residential heating with solid fuels (coal, biomass) and additional regional energy production during winter season.

Carbonates have been known to interfere the thermal carbon analysis by releasing CO_2 at high temperatures. To our knowledge, the integration method, which provides for the exclusion of carbonate from OC in the thermal-optical carbon analysis, is not published earlier. Calcium carbonate had a significant contribution to $PM_{2.5-10}$ concentration in Athens (56%) and Barcelona (11%). This study showed that a simple integration method is a reliable and quantitative tool for the determination of calcium carbonate.

The mean $PM_{2.5}$ mass portions of five OC thermal fractions (OC1, OC2, OC3, OC4 and OCP) varied in the range 26–33%, 6–10%, 7–10%, 9–22% and 29–50%, respectively, in six cities. The differences in the mass portion profiles were relatively small between the cities. The inverse correlation between OC and OC1-OC4 and the good correlation between OC and OCP indicated that the temperature steps of the TOA method used in this study were too short for the 3- or 4-days $PM_{2.5}$ samples.

The on-going toxicological studies will clarify the health significance of these findings.

Acknowledgements. This study was conducted within the framework of the project ‘Chemical and biological characterisation of ambient air coarse, fine, and ultrafine particles for human health risk assessment in Europe’ (PAMCHAR) co-ordinated by the National Public Health Institute of Finland (<http://www.pamchar.org/>). The financial support of the EC-FP5 Quality of

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Life and Management of Living Resources Programme (Contract QLK4-CT-2001-00423), the Academy of Finland (FINE-contract 201701) and the Centre of Excellence Programme 2002-2007 of the Academy of Finland (Contract 53307) and the National Technology Fund (TEKES, Contract 40715/01) is also highly appreciated.

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Table 1. Experimental parameters of the thermal-optical carbon analysis (TOA) method used in this study and those of two well-known methods (NIOSH and IMPROVE).

Carrier gas	This study	NIOSH ^a	IMPROVE ^a
He-1 (OC1)	310°C, 60 s	310°C, 60 s	250°C, 150 s
He-2 (OC2)	480°C, 60 s	475°C, 60 s	450°C, 150 s
He-3 (OC3)	615°C, 60 s	615°C, 60 s	615°C, 250 s
He-4 (OC4)	900°C, 90 s	870°C, 90 s	
He/O ₂ ^b	550°C, 60 s	550°C, 45 s	550°C, 200 s
He/O ₂ ^b	625°C, 60 s	625°C, 45 s	
He/O ₂ ^b	700°C, 45 s	700°C, 45 s	700°C, 160 s
He/O ₂ ^b	775°C, 45 s	775°C, 45 s	
He/O ₂ ^b	850°C, 45 s	850°C, 45 s	850°C, 200 s
He/O ₂ ^b	920°C, 60 s	890°C, 120 s	

^a Sciare et al. (2003)
^b A mixture of 2% oxygen in helium.

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Table 2. The relations between total particulate and carbonaceous fractions in $PM_{2.5}$ and $PM_{2.5-10}$.

		POM/PM (%)			EC/PM (%)			OC/EC			BU/F-OC ^a (%)
		Mean (SD)	Min	Max	Mean (SD)	Min	Max	Mean (SD)	Min	Max	Mean±SD
$PM_{2.5}$	Duisburg	31 (6)	21	38	9.0 (3.1)	4.7	15	2.7 (0.9)	1.7	5.2	16±7
	Prague	54 (4)	48	60	5.7 (2.7)	1.3	11	8.7 (6.0)	3.6	27	6±2
	Amsterdam	23 (4)	19	29	5.4 (3.4)	1.7	13	4.3 (2.6)	1.2	9.8	12±5
	Helsinki	46 (6)	34	57	8.4 (1.8)	4.5	11	4.0 (0.9)	2.8	6.3	14±3
	Barcelona	21 (11)	8.9	49	7.6 (4.5)	3.1	18	2.1 (0.5)	1.5	3.1	17±3
	Athens	35 (4)	30	47	6.8 (1.4)	4.9	9.4	3.9 (0.9)	2.7	5.4	19±3
$PM_{2.5-10}$	Duisburg	24 (8)	3.4	37	2.9 (1.2)	0.48	5.05	9.1 (9.8)	0.7	39	14±19
	Prague	27 (7)	16	41	5.5 (2.6)	2.2	11	3.9 (1.5)	2.0	7.3	10±5
	Amsterdam	15 (8)	5.6	28	2.3 (1.5)	0.06	5.4	11 (21)	3.4	84	12±3
	Helsinki	15 (4)	11	25	1.6 (0.6)	0.84	2.7	7.1 (2.3)	3.8	13.6	8±3
	Barcelona	10 (6)	2.7	23	1.1 (0.9)	0.15	3.2	9.0 (5.5)	4.1	18.1	9±4
	Athens	24 (3)	19	30	1.0 (0.4)	0.23	1.9	24 (17)	9.5	62	6±1

^a BU/F-OC is the ratio of OC on backup filter to OC on front filter in $PM_{2.5}$

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Table 3. Pearson’s correlation coefficients (r) between the PM mass, POM, and EC in PM_{2.5} and PM_{2.5–10}.

	Duisburg	Prague	Amsterdam	Helsinki	Barcelona	Athens
PM2.5 vs. PM2.5–10	0.280	0.554	–0.128	0.584	0.295	0.717
EC(2.5) vs. EC(2.5–10)	0.524	0.379	0.875	0.810	0.884	0.348
POM(2.5) vs. POM(2.5–10)	0.542	0.661	0.897	0.498	0.824	0.800
PM2.5 vs. EC(2.5)	0.553	0.360	0.664	0.722	0.341	0.405
PM2.5 vs. POM(2.5)	0.844	0.987	0.959	0.897	0.567	0.860
EC(2.5) vs. POM(2.5)	0.672	0.436	0.762	0.790	0.945	0.517
PM2.5–10 vs. EC(2.5–10)	0.352	0.822	0.208	0.696	–0.087	0.470
PM2.5–10 vs. POM(2.5–10)	0.651	0.935	0.263	0.904	–0.073	0.831
EC(2.5–10) vs. POM(2.5–10)	0.198	0.828	0.926	0.813	0.870	0.659

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Fig. 1. The locations of six sampling sites in Europe (Map © Genimap).

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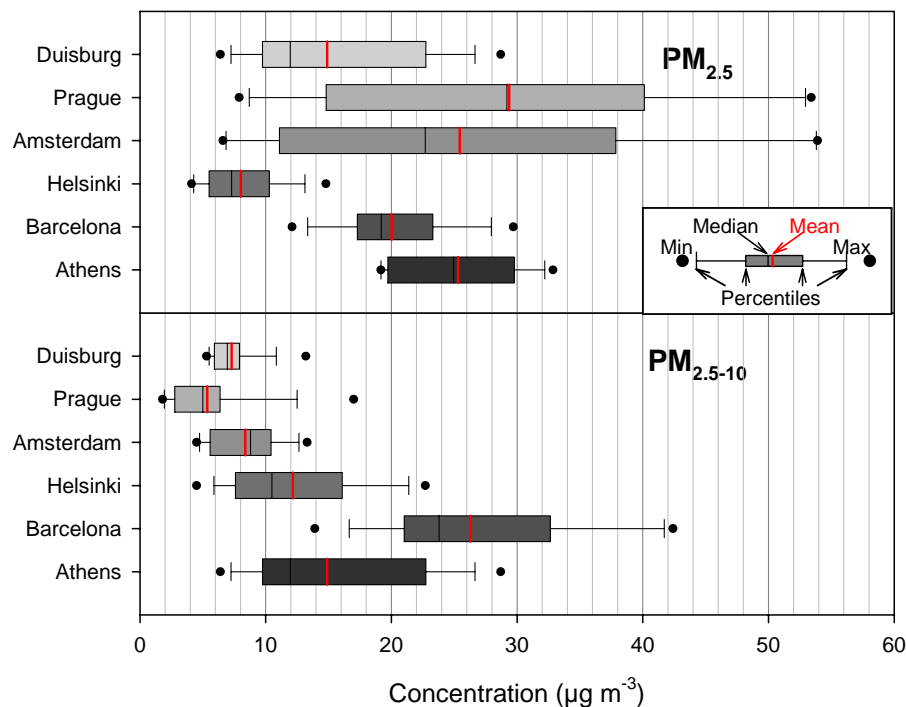


Fig. 2. The mean, median and range as well as percentiles of fine and coarse particulate matter in six cities.

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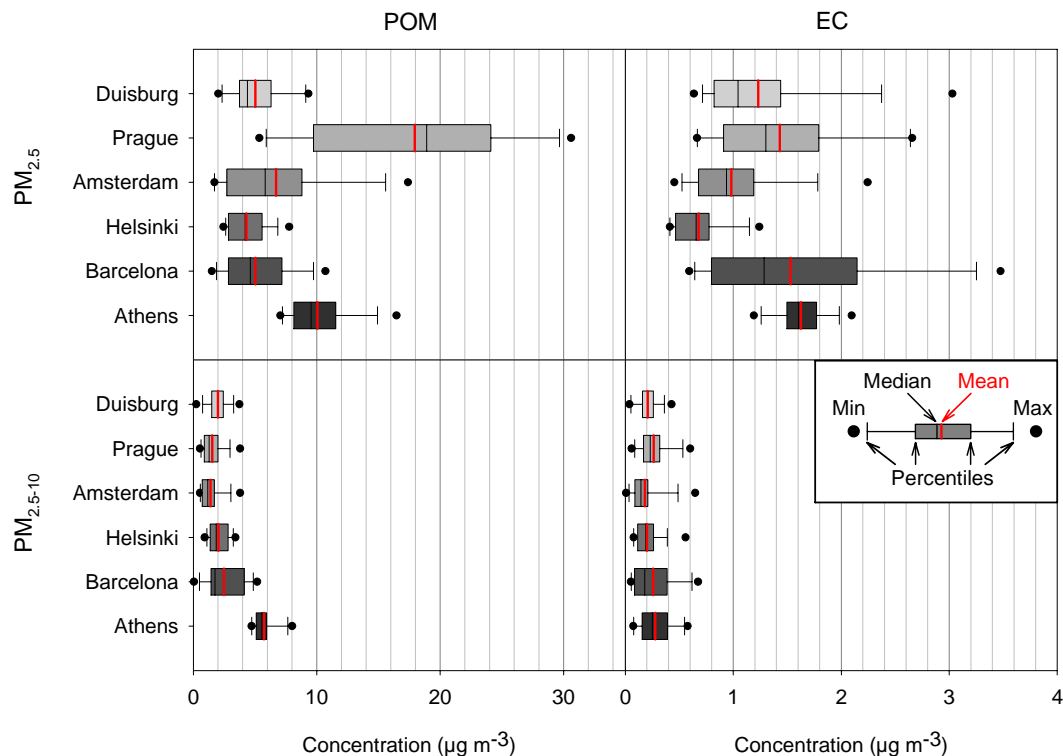


Fig. 3. The mean, median and range as well as percentiles of fine and coarse particulate organic matter and black carbon in six cities.

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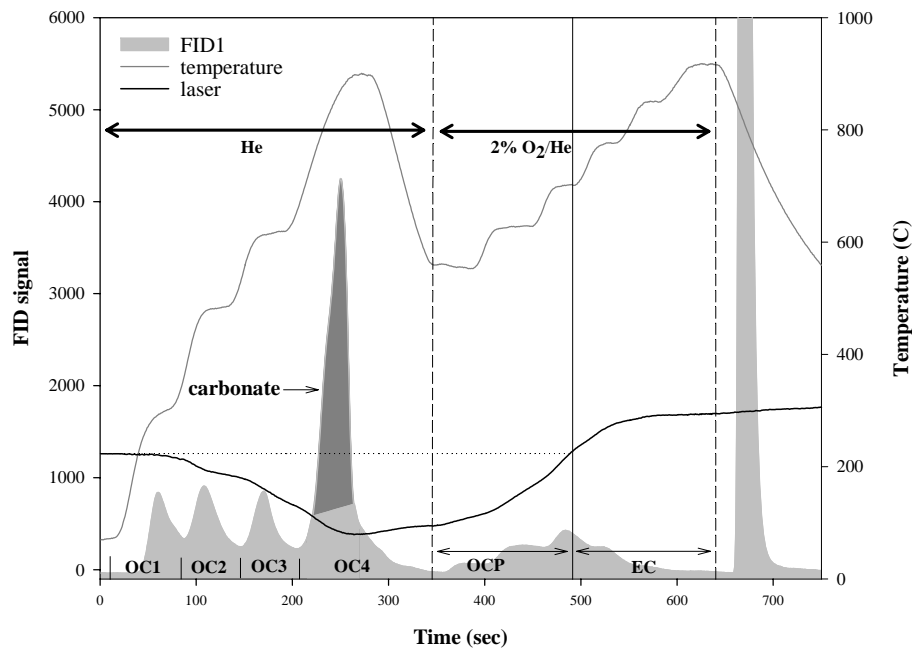


Fig. 4. The temperature program of TOA method used in this study and the manually integrated carbonate peak (coarse sample #14 of Athens).

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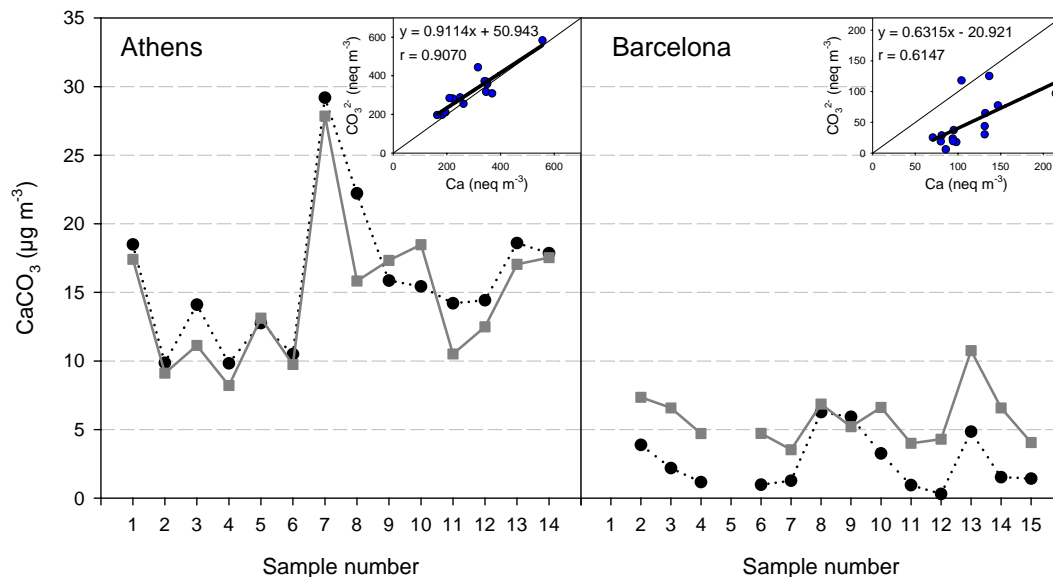


Fig. 5. The concentration of coarse CaCO₃ in PM_{2.5–10} from Athens and Barcelona. The black dotted line is based on the CO₃²⁻ analysed by the TOA, and grey line on the Ca²⁺ analysed by the ED-XRF. The trendline for the molar equivalent concentrations of calcium (x axis) and carbonate (y axis) are shown in the right upper corner.

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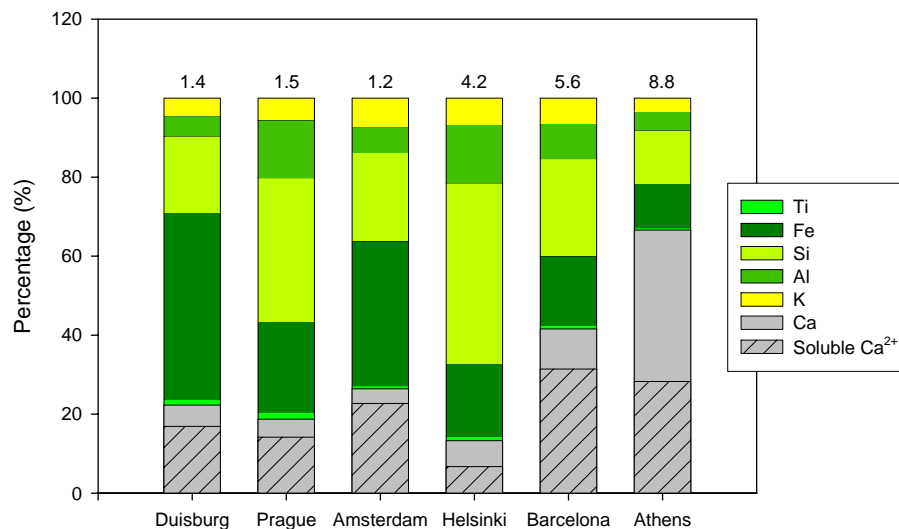


Fig. 6. The proportions of crustal elements (Ca, Ti, Fe, Si, Al and K) in the coarse soil particles. The value above the bar indicates to the sum of mean concentrations ($\mu\text{g m}^{-3}$) of crustal elements. The portion of water-soluble calcium is shown as striped bars.

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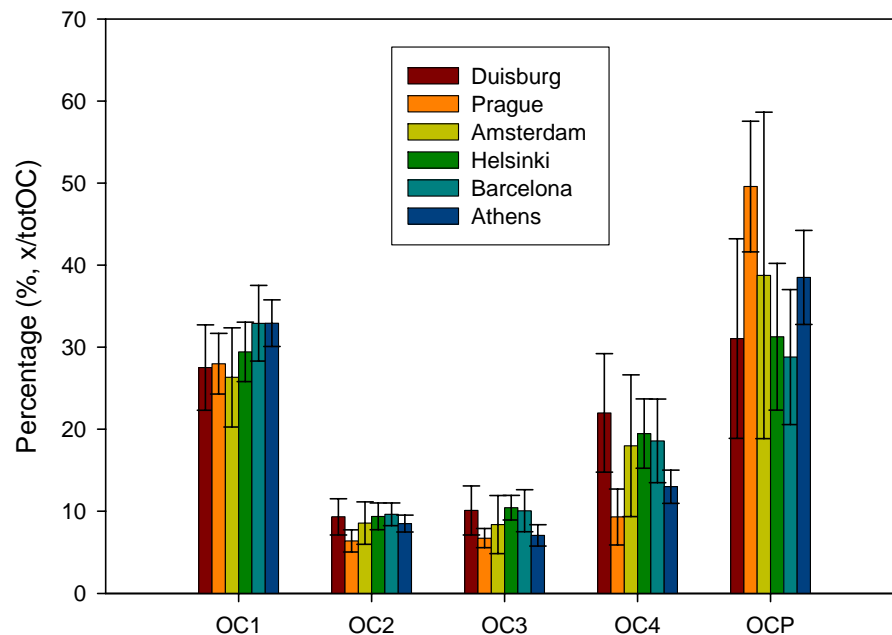


Fig. 7. The mean $PM_{2.5}$ mass portions of five OC thermal fractions in the six-city samples.

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